Dual Luminescence from a Mixed-metal Complex Containing Rhenium(I) and Ruthenium(II) Photochromophores

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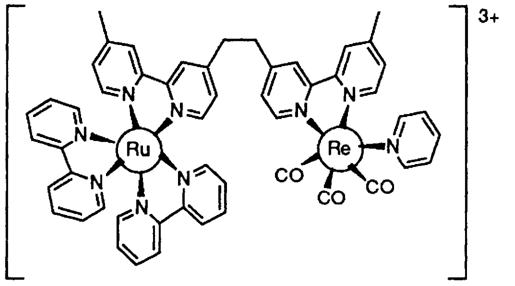
Photophysical properties of the complex $[(bpy)_2Ru(bpyen)Re(CO)_3(py)]^{3+}$ [bpy = 2,2′-bipyridine; py = pyridine; bpyen = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane], show that the cation luminesces at 540 and 610 nm in methylene chloride at room temperature; the luminescence at 540 nm is derived from the Re luminophore component and that at 610 nm from the Ru luminophore component.

We have studied the development of photocatalysts based on d^6 and d^8 transition metal complexes. Previously, we have reported the synthesis and properties of a variety of multimetallic systems containing ruthenium(II)/ruthenium(II),[1] rhenium(I)/rhenium(I),[2] ruthenium(II)/rhenium(I),[3] and ruthenium(II)/platinum(II).[4] We have searched for mixed-metal systems which would display multiple emission in order to demonstrate energy or electron transfer between excited states. To this end, we have isolated $[(bpy)_2Ru(bpyen)Re(CO)_3(py)][PF_6]_3$ (**1**) [py = pyridine; bpyen = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane; bpy = 2,2′-bipyridine]. When excited at 355 nm in methylene chloride, the compound exhibits two distinct excited-state emissions, one associated with the Ru centre and the other associated with the Re centre. While multiple excited-state emission from the same compound is not uncommon, *e.g.*, fluorescence and phosphorescence, we believe that this is the first example of a

$$[(bpy)(bpy^-)Ru^{III}(bpyen)Re^{I}(CO)_3(py)]^{3+*}$$
$$h\nu \uparrow \downarrow h\nu' = 610\ \text{nm}$$
$$[(bpy)(bpy)Ru^{II}(bpyen)Re^{I}(CO)_3(py)]^{3+}$$
$$h\nu \uparrow \downarrow h\nu' = 540\ \text{nm}$$
$$[(bpy)(bpy)Ru^{II}(bpyen^-)Re^{II}(CO)_3(py)]^{3+*}$$

Scheme 1. The two emitting components.



(1)

complex bearing two different metals in which both are observed to emit.

Complex (**1**) was prepared by the reaction of [(bpyen)Re(CO)$_3$Cl][2] with an equal molar quantity of [(bpy)$_2$Ru(solv)$_2$][PF$_6$]$_2$,[5] where solv = methanol. This afforded the mixed-metal precursor, [(bpy)$_2$Ru(bpyen)Re(CO)$_3$Cl][PF$_6$]$_2$, treatment of which with methanol/AgPF$_6$ followed by pyridine yielded complex (**1**), which was purified by reprecipitation from methylene chloride/hexane. TLC showed no evidence of monometallic impurities. Cyclic voltammetric peaks in MeCN (0.1 M Bu$^n_4$NPF$_6$) were located at +1.78 (irr.), +1.25 (0.06),† −1.36 (0.07), −1.60 (0.11), and −1.81 V (0.08) *vs.* saturated sodium chloride calomel electrode. These are consistent with the redox couples expected for [(bpy)$_2$Ru(bpyen)Re(CO)$_3$(py)]$^{3+}$.

The emission and excitation spectra of this complex in methylene chloride are shown in Figure 1. The emission spectrum consists of a peak at 610 nm and a shoulder at *ca.* 540 nm. These can be assigned as illustrated in Scheme 1 to different metal centres by analogy with the reported luminescence maxima of [Ru(bpy)$_3$]$^{2+*}$ at 613 nm[6] and of [(bpy)Re(CO)$_3$(py)]$^{+*}$ at 558 nm.[7]

The electronic spectra in Figure 2, which compares the spectra of the bimetallic complex and the rhenium monometallic species, were studied by serial dilution and found to obey Beer's law. The rhenium monomer shows little absorbance beyond 400 nm but does display a maximum at *ca.* 355 nm, which appears as a broad shoulder on the ruthenium-based absorption between 355 and 380 nm.

The bimetallic complex retained its integrity upon photolysis in neat methylene chloride, its absorption and luminescence spectra being little changed when a 8.8 × 10^{-6} M solution was irradiated at 355 nm (I_o = 1.8 × 10^{-9} einsteins/mol) for an extended period (> 1 h). The absorption spectrum of the bimetallic complex in Figure 2 could be modelled with a 1:1 mixture of [(bpy)$_2$Ru(bpyen)]$^{2+}$ and [(bpyen)Re(CO)$_3$(py)]$^+$, but not the luminescence spectrum in Figure 1. The latter could more closely be modelled with a 9:1 mixture. Further, room-temperature emission quantum yields determined in freeze-pump-thaw degassed methylene chloride solutions irradiated at 355 nm changed from ϕ_{em} (540 nm) = 0.254 ± 0.005 for [(bpyen)Re(CO)$_3$(py)]$^+$ and ϕ_{em} (610 nm) = 0.139 ± 0.004 for [(bpy)$_2$Ru(bpyen)]$^{2+}$ to ϕ_{em} (540 nm) = 0.011 ± 0.001 and ϕ_{em} (610 nm) = 0.149 ± 0.003 for the bimetallic complex. The fact that the Ru-based emission in the bimetallic complex increases at the expense of the Re-based emission suggests that the mechanism for the process may involve energy transfer similar to the rationale given for excited state quenching in a mixed ligand ruthenium(II) bimetallic complex.[8]

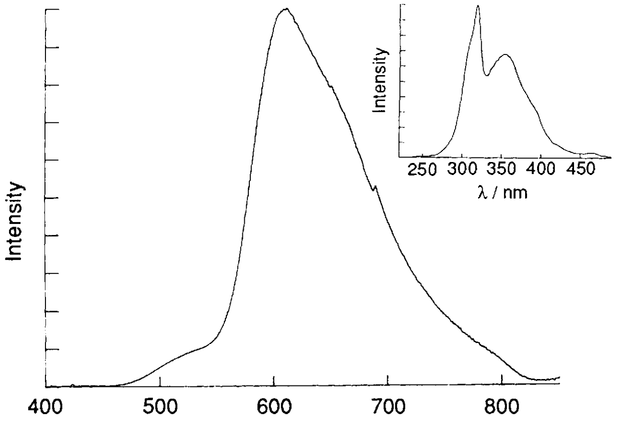


Figure 1. Emission (λ_{ex} 355 nm) and excitation (λ_{em} 533 nm, inset) of complex (**1**) in methylene chloride.

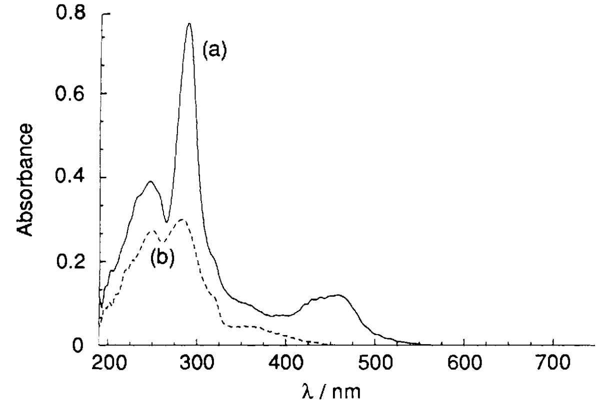


Figure 2. Absorption spectra in CH$_2$Cl$_2$ of: (a) 9.2 × 10^{-6} M complex (**1**); (b) 8.5 × 10^{-6} M [(bpyen)Re(CO)$_3$(py)]$^+$.

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† Value in parentheses is ΔE_p, where $\Delta E_p = (E_{p,\,ox} + E_{p,\,red})/2$.